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14. ABSTRACT We completed work on a series of large self assembled supra-molecular complexes including a square, triangle and prism and demonstrated that our ion mobility methods coupled with high level modeling could yield structures comparable to those obtained using x-ray diffraction. More complex systems are currently being investigated. We also completed the first phase of a new computational paradigm that allows rapid and accurate determination of cross sections from theoretical model structures. The second and final stage of the paradigm is currently nearing completion. This model will allow structural studies using ion mobility to be extended to arbitrarily large systems					
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Final Technical Report

AFOSR GRANT: AF9550-06-1-0069

POSS and Metal Clusters- Structure and Energetics

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SUMMARY OF PROGRESS

During the tenure of the grant we have published 9 papers in peer reviewed journals: 4 on Poly-oligomeric silsesquioxane cage systems (POSS), 2 involving metal clusters, one on the completion of a new high resolution ion mobility instrument, one on self assembled supramolecular systems and one on a new paradigm for computing cross sections of large complex molecules and aggregates. In order to accomplish this work we have collaborated with Dr. Tim Haddad at Edwards AFB, Prof. E. Bryan Coghlin at the University of Massachusetts, Dr. Arpad Somogi at the University of Arizona and Prof. Peter Stang at the University of Utah. All of this work has been described in detail in the 9 papers that have been cited in this and past reports.

One important point should be emphasized that is not commented on in detail in the Annual Reports or the various published papers. Based on the great success of the very high resolution ion mobility instrument we designed and built with AFOSR funds (primarily a DURIP but also funds from this grant to complete the work) we have successfully formed a collaboration with an Instrument Manufacturing Company to design and build an upgraded version of this instrument for commercial sale. The new paradigm for calculating cross sections of very large systems also played a key role in this process since it allowed the experimental horizon to be expanded. We have successfully built two prototypes of the instrument in our lab which couples our technology with the companies and built a third unit that was shipped to the Instrument Company for their engineers to streamline into a commercial model. Since public funds were used for our work I have turned down any personal remuneration but have negotiated a small royalty from each sold instrument to be used to support our research. A good deal of the success of this venture is due to the generous AFOSR support my group has received over the years.

Finally during the tenure of this grant AFOSR has supported completely or in part 3 senior research personnel, 2 post docs, 3 PhD students and 2 undergraduates as well as contributed to the remainder of my research program through shared equipment and other resources such as computing.

New Work
Projected 2009-2010
Grant AFOSR FA9550-06-01-0069

In what follows I will briefly outline work we intend to pursue through 2010. Normally I would do a thorough documentation of each point along with any preliminary results obtained and goals associated with each project. Here these areas will be significantly compressed due to the nature of this document. Essentially all of the work described will be POSS related. We will clean up a couple of projects dealing with metal clusters and will consider a new effort in metal oxide clusters. These latter species are receiving significant attention as new catalytic agents yet little is known about their structural and reactive properties. There is interest (along with my colleagues Steve Buratto and Horia Metiu) in depositing selected metal oxide clusters on both metal oxide and metallic surfaces and the structure of the species before desorption would be an important parameter, as would comparing the reactivity of free and deposited clusters. However, at this point the project is still in the design stage and so specific systems won't be outlined here although if we proceed, vanadium oxide clusters, both cationic and anionic, will be our first targets.¹

What follows is a very brief summary of several POSS related projects we will definitely be pursuing in the near future. I won't explicitly mention the application of our new high-resolution instrument but we fully intend to use it on virtually all systems described here.

1. F⁻ and POSS oligomers

Following the success of our fluoridation of POSS monomers, we will attempt to extend this work to various oligomers. In principle this appears simple but the fluoridating agent (CH_3)₄NF, or TMFA, cleaves the backbone of methacrylate oligomers so an all-carbon backbone will be required. Our initial efforts will focus on POSS styrenyl polymers but a number of other systems are under consideration as well. The key idea here is to provide

an ionic tag that minimally disrupts the oligomer structure so we can investigate how these POSS polymers fold.

2. New fluorophenyl-based matrices

We strongly suspect that one of the principle reasons we see diminished intensity as oligomer number increases is the cationization process becomes less efficient using our standard MALDI matrices like dihydroxybenzoic acid. We have been collaborating with Dr. Arpad Somogyi at the University of Arizona on new matrix

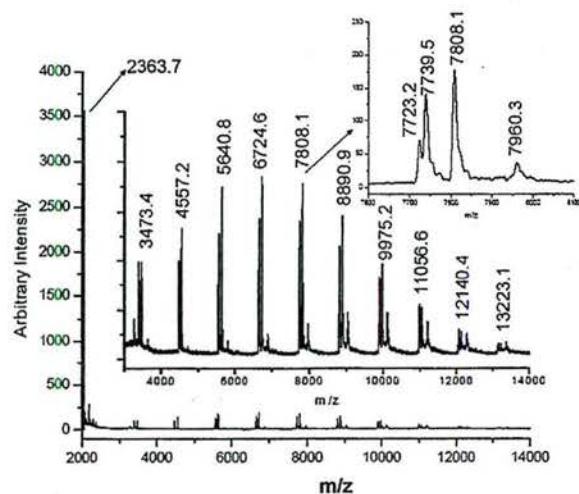


Figure 2. Phenyl POSS PMA MALDI mass spectrum using DHFAB matrix. Typical series shown in expansion in region of $m/z = 7800$

The dominant peaks in this spectrum are oligomers cationized by Na^+ and K^+ . Satellite peaks are due to end group loss (Br) and other minor fragmentation processes. This is a very positive result and we will hopefully be using this matrix soon in studies at UCSB. Prof. Bryan Coughlin at UMASS has sent us a series of POSS PMA and POSS styrenyl oligomers to try with this new matrix.

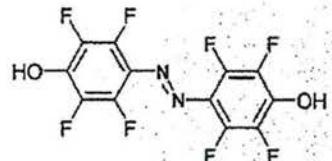


Figure 1. 4,4'-Dihydroxyoctofluoroazobenzene (DHFAB)

development. His idea is to use the powerfully solvating tetrafluorophenyl group to solvate our POSS oligomers and couple this group with an azo group to absorb the UV light. He has generated a number of such materials²⁻⁴ and the one we are focusing on is the 4,4'-dihydroxyoctofluoroazobenzene (DHFAB) shown in Figure 1. We have obtained preliminary data on a family of phenyl POSS PMA oligomers using DHFAB (Figure 2).

3. Fluoro POSS materials

Fluoro POSS materials continue to be of interest to the Air Force as low-surface-energy species.⁵⁻⁷ Hydrophobic and oleophobic properties are important for many gasket, seal and wing structure applications. Here we intend to look at fluoro POSS oligomers generated as shown in Figure 3.

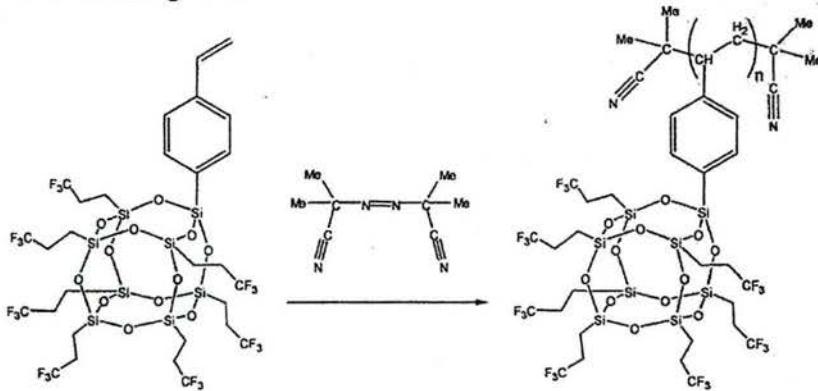


Figure 3. Oligomeric POSS styrenes with fluoropropyl capping groups.

Similar materials based on POSS PMA will also be investigated. The monomer in Figure 3 has now been synthesized and a family of oligomers will be made by Tim Haddad at Edwards AFB for us to investigate.

4. POSS Diamines

POSS polyimide (Kapton-like) materials are orders of magnitude more chemically resistant to high-energy particles and atomic oxygen than polyimides themselves.⁶⁻¹⁰ Possible important building blocks for these materials are third and fourth generation POSS diamines shown in Figure 4.

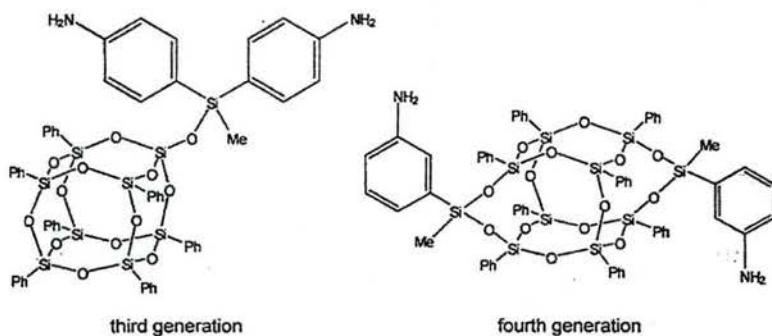


Figure 4. Third and fourth generation diamine monomers.

They are many synthetic routes to polymer formation using these monomers that are being developed. Of interest is the fact that the POSS moiety will dangle from the polymer backbone when made from third generation systems and will be part of the backbone in fourth generation systems. Again the synthesis will be carried out by Tim Haddad at Edwards AFB.

5. Other systems

The systems mentioned above are already being actively pursued by our synthetic collaborators. Of course there are other possibilities that may also develop in the course of our research. One non POSS possibility is the so-called Q₄ ring systems composed of cyclic (SiO)₄. A variety of O-R substituents can be attached to the reactive Si centers on the ring. So far the Haddad group has succeeded for R = CH₃, vinyl or several fluoroalkyl species but not for R = H. The idea is to oligomerize these systems for addition to polymer composites. Nothing is known about oligomer structures which should make this work both interesting and challenging.

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